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EFFECTS OF HOT CORROSION ON THE ROOM TEMPERATURE STRENGTH OF STRUCTURAL CERAMICS

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ABSTRACT

A variety of advanced structural ceramics were treated in air at 1000°C for 500 hours with and without various amounts of sodium sulfate. Room temperature flexure strength was determined before and after treatments. Results show that Ce-TZP and alumina are resistant to strength degradation after exposure to sodium sulfate, however Si_3N_4 and, to a lesser degree, Y-TZP are not.

The Y-TZP had a strength loss of $\approx 25\%$ after 500 hours at 1000°C with 10 to 20 mg/cm^2 of Na_2SO_4. This loss is about 10% greater than that experienced by specimens when treated at 1000°C for 500 hours without sodium sulfate present, and is probably due to the leaching of Y_2O_3 from the zirconia which allows the tetragonal zirconia to transform to the monoclinic phase. Under similar conditions, the silicon nitride experienced a loss of $\approx 65\%$ when sodium sulfate was added. This strength loss is $\approx 25\%$ greater than the loss after thermal exposure in the absence of sodium sulfate. The additional strength loss here is due to the formation of larger corrosion pits.

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INTRODUCTION

The service environments projected for structural ceramics are quite hostile. In the gas turbine engine, some of the structural ceramics will face hot corrosion: the attack by molten Na_2SO_4 (Tm = 884°C) which condenses on engine parts when ingested NaCl reacts with sulfur impurities in the fuel. Marine propulsion gas turbine engines experience a similar lower temperature sulfate-induced corrosion. How long-term exposure to these corrosive environments affects the mechanical properties of ceramics is of critical importance to their successful application in engines as high temperature structural components.

Although, at the present time, monolithic tetragonal zirconia polycrystal ceramics (TZPs) are not being considered for structural applications such as gas turbine blades and other components in the high temperature regions (>1000°C) of gas turbine engines, this does not preclude the use of composites based on a TZP matrix from finding application in this environment. Moreover, the use of zirconia ceramics in nonstructural applications in the high temperature region of gas turbines appears inevitable (e.g., thermal barrier coatings, etc.). Thus, the effect of hot corrosion on the mechanical properties of TZPs may have important technological implications. On the other hand, Si_3N_4 ceramics are being considered and, in certain applications, incorporated as monolithic components in advanced engines.

The actual mechanisms of hot corrosion in TZPs[1-5] and Si_3N_4[6-12] have been studied. However, there has been little work examining the interactions between hot corrosion and mechanical properties. Important properties that may be affected by hot corrosion are room temperature and elevated temperature strength, toughness, and creep-rupture behavior.

This report provides a review of the mechanisms of hot corrosion, and presents results on the effect of hot corrosion on the room temperature strength of two TZPs and a Si_3N_4. A high purity alumina ceramic has also been examined for comparison.

LITERATURE REVIEW

Formation of Sodium Sulfate in Engines

One of the Army's important long-range goals is to develop engines with the ability to handle alternate fuels (i.e., various grades of gasoline, diesel, and shale oil or coal-derived

1. HAMILTON, J. C., and NAGELBERG, A. S. *In Situ Raman Spectroscopic Study of Yttria-Stabilized Zirconia Attack by Molten Sodium Vanadate.* J. Am. Ceram. Soc., v. 67, no. 10, 1984, p. 686-690.

2. BARKALOW, R., and PETTIT, F. *Mechanisms of Hot Corrosion Attack of Ceramic Coating Materials.* Proceedings of 1st Conference on Advanced Materials for Alternative Fuel Capable Directly Fired Heat Engines, CONF-790749, J. W. Fairbanks and J. Stinger, ed., NTIS, Springfield, VA, 1979, p. 704-710.

3. JONES, R. L., NORDMAN, D. B., and GADOMSKI, S. T. *Sulfation of Y_2O_3 and HfO_2 in Relation to MCrAl Coatings.* Metall. Trans., v. 16A, no. 2, 1985, p. 303-306.

4. JONES, R. L., JONES, S. R., and WILLIAMS, C. E. *Sulfation of CeO_2 and ZrO_2 Relating to Hot Corrosion.* J. Electrochem. Soc., v. 132, no. 6, 1985, p. 1498-1501.

5. NAGELBURG, A. S. *Destabilization of Yttria-Stabilized Zirconia Induced by Molten Sodium Vanadate-Sodium Sulfate Melts.* J. Electrochem. Soc., v. 132, no. 10, 1985, p. 2502-2507.

6. TRESSLER, R. E., MEISER, M. D., and YONUSHONIS, T. *Molten Salt Corrosion of SiC and Si_3N_4 Ceramics.* J. Am. Ceram. Soc., v. 59, no. 5-6, 1976, p. 278-279.

7. LEVY, M., and FALCO, J. *Hot Corrosion of Reaction-Bonded Si_3N_4.* Am. Ceram. Soc. Bull., v. 57, no. 4, 1978, p. 457-458.

8. BOURNE, W. C., and TRESSLER, R. E. *Molten Salt Degradation of Si_3N_4 Ceramics.* Am. Ceram. Soc. Bull., v. 59, no. 4, 1980, p. 443-452.

9. SMIALEK, J. L., FOX, D. S., and JACOBSON, N. S. *Hot Corrosion Attack and Strength Degradation of SiC and Si_3N_4.* Prepared for NASA-Lewis Research Center for the Environmental Degradation of Engineering Materials III, NASA TM-89820, April 13-15 1987.

10. JACOBSON, N. S., and FOX, D. S. *Molten Salt Corrosion of Silicon Nitride: II. Sodium Sulfate.* J. Am. Ceram. Soc., v. 71, no. 2, 1988, p. 139-148.

11. JACOBSON, N. S., SMIALEK, J. L., and FOX, D. S. *Molten Salt Corrosion of SiC and Si_3N_4.* Prepared for NASA-Lewis Research Center, NASA TM-101346, November 1988.

12. DAVIES, G. B., HOLMES, T. M., and GREGORY, O. J. *Hot-Corrosion Behavior of Coated Covalent Ceramics.* Adv. Ceram. Mat., v. 3, no. 6, 1988, p. 542-547.

fuels) without requiring physical adjustments to the engine or compromising engine performance and life.[13] Low grades of these fuels commonly contain parts per million of one or more of the following: Na, S, K, and V. During the combustion process, reactions can occur involving these impurities, creating a material which can lead to corrosion of the engine components.

This report is concerned with the corrosion by sodium sulfate. Sodium sulfate (Na_2SO_4) is formed and condenses on engine components when sodium, ingested from fuel impurities or a marine environment, reacts with sulfur impurities in the fuel according to the following reaction:

$$2NaCl \text{ (g)} + SO_2 \text{ (g)} + 1/2O_2 \text{ (g)} + H_2O \text{ (g)} = Na_2SO_4 \text{ (1)} + 2 HCl \text{ (g)}.^{14} \qquad (1)$$
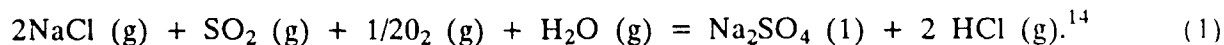
Typically, corrosion is only a problem between the melting point and the dew point of the corrosive material, since in this temperature range the material is fluid and can rapidly spread, enhancing the corrosion process. Below the melting point, transport is too slow, thus, the rate of corrosion is very limited. Above the dew point, thermodynamics inhibit the formation of the corrosive medium due to evaporation. However, higher pressures increase the dew point and, thus, the temperature range in which corrosion is possible. Since advanced engines are expected to operate at higher temperatures and pressures, an understanding of the corrosion mechanisms in ceramics and the effects on mechanical properties are important.

Interaction of Zirconia and Its Stabilizers with Sodium Sulfate

The formation of TZP materials is possible due to the high solubility of yttria (Y_2O_3) and ceria (CeO_2) in zirconia. These oxides act to stabilize the tetragonal grains against the tetragonal-to-monoclinic transformation which occurs in pure zirconia. This allows for the production of a zirconia material which is essentially 100% tetragonal, having an unusual combination of high strength and toughness. Because of these excellent properties, TZP materials have been extensively examined for potential use in advanced engines.[15-18]

These stabilizing oxides limit the hot corrosion resistance of TZPs. Both oxides can undergo a sulfation reaction which effectively "leaches" the oxide from the TZP, causing surface destabilization and property degradation. Barkalow and Pettit[2] first proposed that Y_2O_3 is leached from a TZP by the sulfation reaction in Equation 2.

$$Y_2O_3 + 3SO_3 = 2Y^{+3} + 3SO_4^{-2} \qquad (2)$$
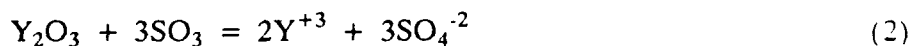
This reaction is dependent on the partial pressure of SO_3. They showed that at 700°C, a SO_3 partial pressure of only 70 Pa was required for the forward reaction to occur.

13. GLANCE, P. C., and MUNT, R. *Engine Research, Development, and Acquisition Strategy for US Army Group Vehicles.* SAE Paper 830674. SAE International Congress and Exposition, Detroit, MI, 1983, p. 1-13.
14. KOHL, F. J., STEARNS, C. A., and FRYBURG, G. C. *Sodium Sulfate: Vaporization and Role in Corrosion Flames.* Metal-Slag-Gas Reactions and Processes, Z. A. Foroulis and W. W. Smeltzer, ed., The Electrochemical Society, Pennington, NJ, 1975, p. 649.
15. SWAB, J. J. *Properties of Yttria-Tetragonal Zirconia Polycrystal (Y-TZP) Materials After Long Term Exposure to Elevated Temperatures.* U.S. Army Materials Technology Laboratory, MTL TR 89-21, March 1989, Prepared for the U.S. Department of Energy under Intergency Agreement DE-AIO5-84OR-21411.
16. LARSEN, D. C., and ADAMS, J. W. *Long-Term Stability and Properties of Zirconia Ceramics for Heavy Duty Diesel Engine Components.* Prepared for NASA-Lewis Research Center, for U.S. Department of Energy under Contract DEN 3-305 NASA CR-174943, September 1985.
17. SCHIOLER, L. J. *Effects of Time and Temperature on Transformation Toughened Zirconias.* U.S. Army Materials Technology Laboratory, MTL TR 87-29, June 1987, Prepared for U.S. Department of Energy under Interagency Agreement DE-AIO5-84OR-21411.
18. HECHT, N. L., McCULLUM, D. E., GRANT, D. W., WOLF, J. D., GRAVES, G. A., and GOODRICH, S. *The Experimental Evaluation of Environmental Effects in Toughened Ceramics for Advanced Heat Engines.* Proceedings of the 23rd Automotive Technology Development Contractors' Coordination Meeting, Dearborn, MI, October 1985, Society of Automotive Engineers, Warrendale, PA, March 1986, p. 299-310.

Later work[3] confirmed the high reactivity of Y_2O_3 with SO_3 yielding a similar reaction which suggests $Y_2O_2(SO_4)$ or $Y_2(SO_4)_3$ as the sulfation products. Tests at 700°C showed that Y_2O_3 was so reactive that the equilibrium partial pressure of SO_3 could not be measured with their equipment. Further tests at 850°C, 900°C, and 900°C yielded SO_3 partial pressure of 1.5, 2.5, and 3.5 Pa, respectively.

Jones et al.[4] examined the sulfation of CeO_2 and ZrO_2. They concluded that the sulfation of CeO_2 follows Equation 3

$$CeO_2 \text{ (s)} + SO_3 \text{ (g)} = CeOSO_4 \text{ (s)} \tag{3}$$
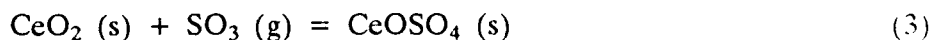
and at 650°C, 700°C, and 750°C, the equilibrium partial pressure of SO_3 is 30, 100, and 230 Pa, respectively. Extrapolation of the thermodynamic data from Equation 3 yields a partial pressure of ~1200 Pa at 850°C for the sulfation of CeO_2.

The examination of ZrO_2 indicated that it is difficult to sulfate. It remains essentially unsulfated at SO_x partial pressures of ~1000 Pa at 700°C. Therefore, the hot corrosion resistance of TZP materials will be dependent on the stabilizers rather than the zirconia. Of the two common stabilized TZPs, the thermodynamic data indicates that CeO_2 stabilized ZrO_2 will be more resistant to corrosion by Na_2SO_4 than the Y_2O_3 stabilized ZrO_2.

Interaction of Silicon Nitride with Sodium Sulfate

Silicon-based ceramics rely on a thin layer of SiO_2 for protection against oxidation. The degradation of Si_3N_4 at high temperatures in a corrosive environment is believed to be due to the dissolution of this protective layer. Jacobson et al.[11] completed a comprehensive literature survey of the corrosion of silicon-based ceramics with the conclusion that in the presence of Na_2SO_4, Na_2O is the key reactant in the corrosion process. Sodium sulfate dissociates according to Equation 4

$$Na_2SO_4 \text{ (l)} = Na_2O \text{ (s)} + SO_3 \text{ (g)} \tag{4}$$
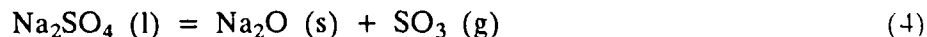
with the Na_2O formed then reacting with the SiO_2 protective layer to form a sodium-silicate glass, Equation 5,

$$xSiO_2 \text{ (s)} + Na_2O \text{ (s)} = Na_2O \text{ } x(SiO_2)^1 \tag{5}$$
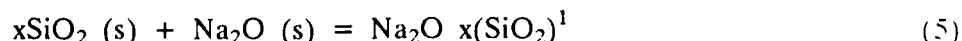
which allows for extensive corrosion of the ceramic. Equation 5 is controlled by the activity of Na_2O. A high $a[Na_2O]$ is considered a basic molten salt while a low $a[Na_2O]$ is termed an acidic molten salt. It has been shown[10,11] that at 1000°C, when the $a[Na_2O]$ is below 10^{-10}, the reaction in Equation 5 does not proceed, indicating that dissolution and corrosion will only occur when the $a[Na_2O]$ is high enough to be considered a basic molten salt. As a note, from Equation 4 it can be seen that the $a[Na_2O]$ will be dependent on the partial pressure of SO_3. In the engine, this pressure will depend on the operating temperature and amount of sulfur in the fuel. Thus, the $a[Na_2O]$ and, ultimately, the corrosion behavior of the silicon-based ceramic will vary with the engine environment.

EXPERIMENTAL PROCEDURE

Four commercially available ceramics, a yttria-TZP, a ceria-TZP, a silicon nitride, and an alumina (see Table 1) were obtained and machined into bend bars 3 x 4 x 50 mm long. The bars were carefully ground by a surface grinder such that the surface striations were parallel to the long axis. All four long edges were chamfered ~45° to a depth of ~0.15 mm; the bars were machined according to Reference 19. A minimum of 5 bars from each ceramic were used to determine the as-received room temperature strength. They were broken in 4-point flexure according to MIL-STD-1942(MR), with inner and outer spans of 20 mm and 40 mm, respectively, and a cross-head speed of 0.5 mm/min.

Table 1.

Material	Manufacturer	Code	Process	Additives	Grain Size (μm)
Y-TZP	NGK Insulators	Z-191	Sintered	Y_2O_3	0.3
Ce-TZP	Ceramatec	CZ203	Sintered	CeO_2/Al_2O_3	1.2
Si_3N_4	Norton	NC-132	Hot Pressed	MgO	3-6
Al_2O_3	Coors Ceramics	AD-999	Sintered	None	3-6

Three other groups of 5 bars from each ceramic were then subjected to one of the following treatments:

- 500 hours at 1000°C with no Na_2SO_4

- 500 hours at 1000°C with 10 to 20 mg/cm^2 of Na_2SO_4

- 500 hours at 1000°C with 50 to 75 mg/cm^2 of Na_2SO_4

Sodium sulfate was applied by mixing anhydrous sodium sulfate (Na_2SO_4) with distilled water then applying the solution to one 4-mm by 50-mm face of each bar. The solution was limited to a centered 30-mm span of the face. The bars were then heated using a hot plate, driving off the water, and leaving behind a layer of Na_2SO_4. The weight of each bar was measured before and after application of the coating to ensure that the amount was in the specified range. Tensile surfaces of each material from each condition were analyzed for phase changes by X-ray diffraction using CuKα radiation.

Heat treatments were done in air, at laboratory ambient humidity (40% to 60%), with the specimens supported in an unstressed condition on silicon carbide knife edges to ensure uniform heating. The knife edges supported the compressive surface of the bar well outside the area to be tested during 4-point flexure testing. The surface with the Na_2SO_4 was placed face-up during the heat treatments to minimize any loss of the Na_2SO_4. Once the strength was determined, the fracture surface of each bar was examined optically at low magnification, and a scanning electron microscope (SEM) was employed for high magnification examination of selected fracture surfaces to determine cause of fracture.

19. *Flexure Strength of High-Performance Ceramics at Ambient Temperatures.* Department of the Army MIL-STD-1942. 21 November 1983

RESULTS AND DISCUSSION

The results of the room temperature flexure strength testing, Figure 1, show the Ce-TZP to be the most resistant to strength degradation after exposure to molten sodium sulfate at 1000°C, followed by the alumina and the Y-TZP. The Si_3N_4 shows the largest strength loss after exposure.

MEAN ROOM TEMPERATURE STRENGTH (MPa)
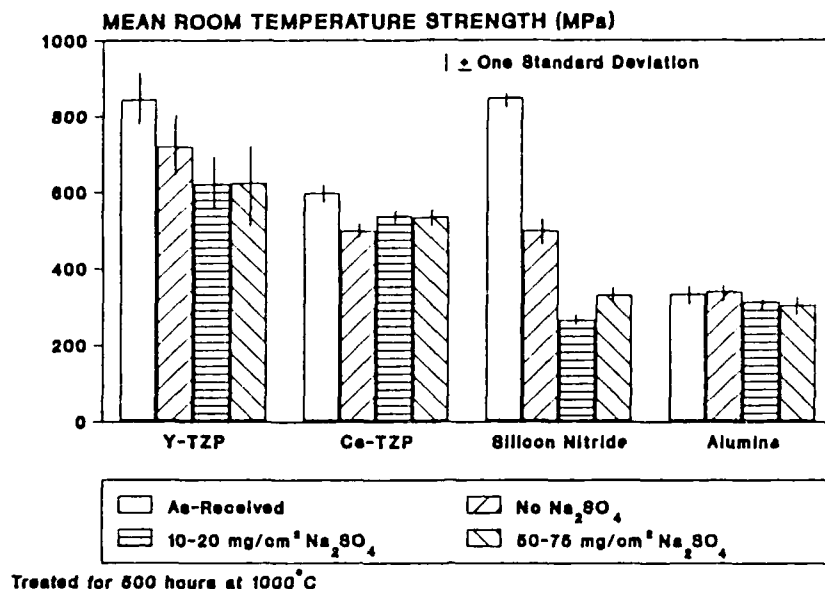
Figure 1. Mean room temperature strength after corrosion with and without sodium sulfate.

The slight strength reduction of the Ce- and Y-TZP after 500 hours at 1000°C without Na_2SO_4 can be attributed to the fact that these materials are transformation-toughened ceramics and are susceptible to overaging when exposed to elevated temperatures for a prolonged time. The addition of a small amount of a rare earth oxide, such as CeO_2 or Y_2O_3, along with an appropriate processing technique, allows for the retention of metastable tetragonal zirconia at room temperature. However, when overaging occurs, the tetragonal zirconia transforms to the stable monoclinic phase, resulting in a reduction in strength.[15-18]

The Si_3N_4 has a significantly large reduction in strength (~40%) when exposed to the same treatment conditions. An oxidized layer of SiO_2 forms when Si_3N_4 is exposed to temperatures in excess of 1000°C for a prolonged time[20,21] (Figure 2b). The loss of strength is due to the creation of oxidation pits as shown in Figure 3b. Alumina does not undergo phenomena such as these. Thus, there is no reduction in strength as a result of this exposure.

The addition of Na_2SO_4 to the long time/high temperature exposures does not cause any further strength reduction in the Ce-TZP, and only minimal reduction in the alumina. However, the Y-TZP and, to a greater extent, the Si_3N_4 experience significant reductions in strength.

20. FREIMAN, S. W., MECHOLSKY, J. J., McDONOUGH, W. J., and RICE, R. W. *Effect of Oxidation on the Room Temperature Strength of Hot-Pressed Si_3N_4+MgO and $Si_3N_4+ZrO_2$* in Ceramics for High Temperature Performance Applications - II, J. J. Burke, E. N. Lenoe, and R. N. Katz, ed., Brook Hill Publishing, 1978, p. 1069-1076.

21. EVANS, A. G., and DAVIDGE, R. W. *The Strength and Oxidation of Reaction-Bonded Silicon Nitride.* J. Mat. Sci., v. 5, 1970, p. 314-325.
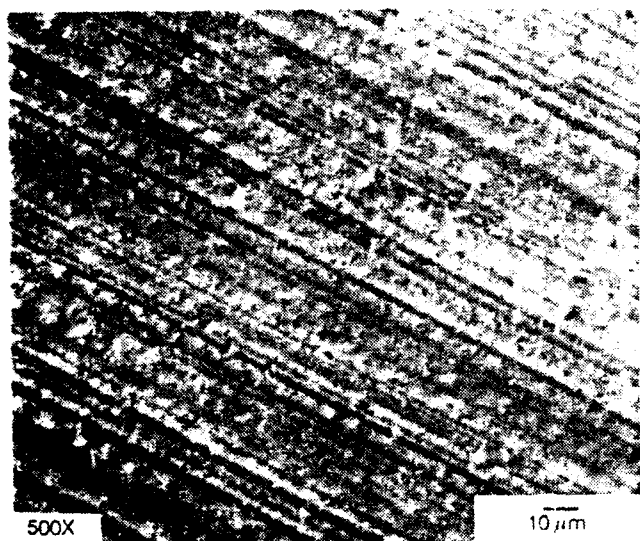
(a) As-Received
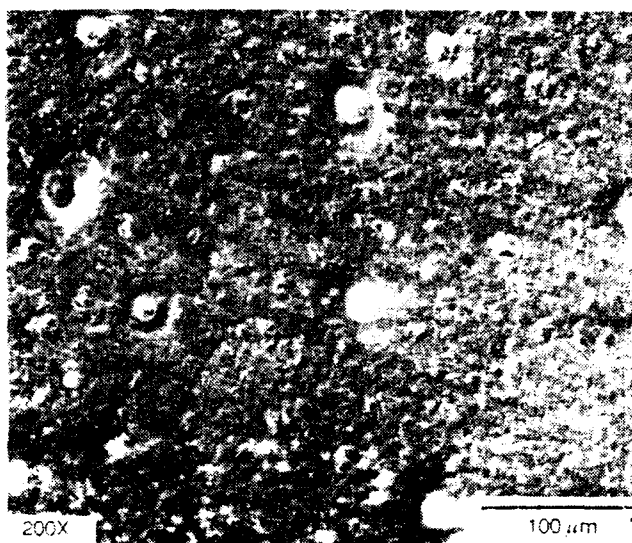
(b) After 500 Hours at 1000°C without Na₂SO₄
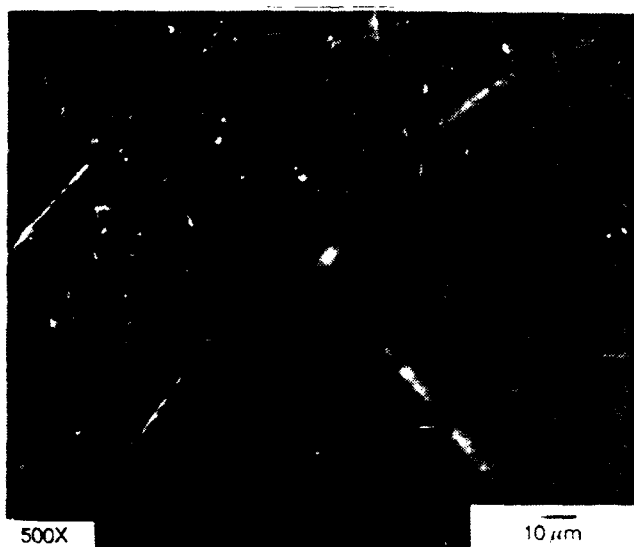
(c) After 500 Hours at 1000°C with 10 to 20 mg/cm² Na₂SO₄
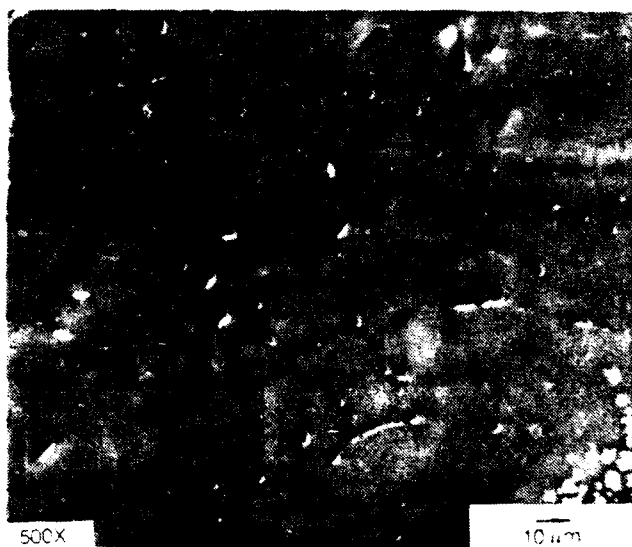
(d) After 500 Hours at 1000°C with 50 to 75 mg/cm² Na₂SO₄

Figure 2. Tensile surfaces of Si₃N₄.

6
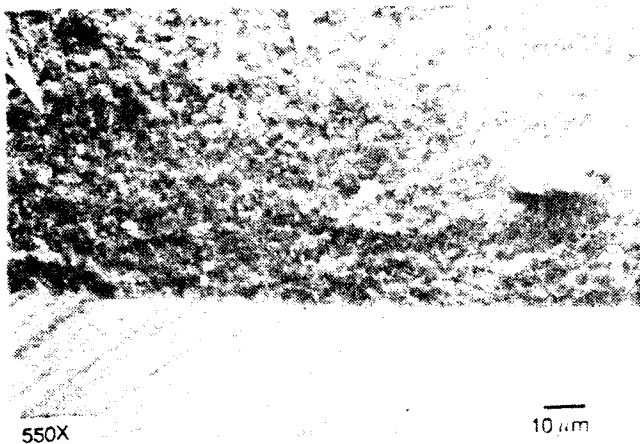
(a) As-Received - Machining Damage
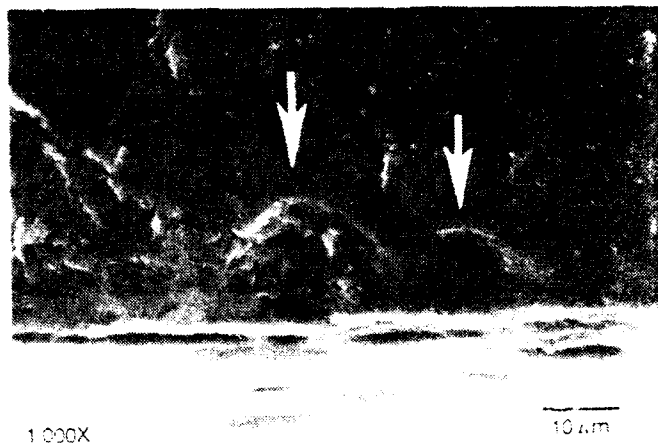
(b) After 500 Hours at 1000°C without Na_2SO_4 - Oxidation Pits
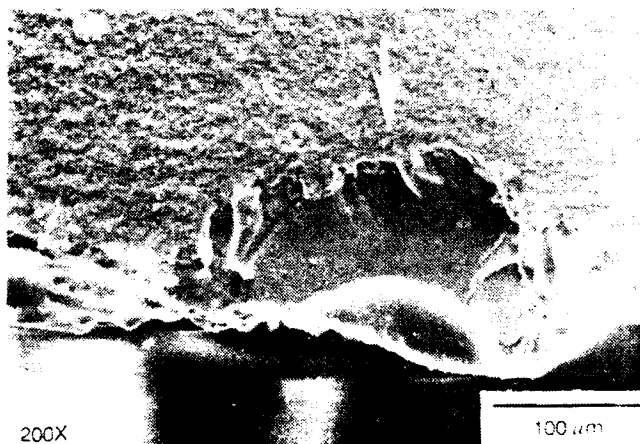
(c) After 500 Hours at 1000°C with 10 to 20 mg/cm^2 Na_2SO_4 - Corrosion Pits

(d) After 500 Hours at 1000°C with 50 to 75 mg/cm^2 Na_2SO_4 - Corrosion Pits

Figure 3. Fracture orgins of silicon nitride. Note the change in magnification from (a) and (b) to (c) and (d).

As previously mentioned, it has been shown[2] that Y_2O_3 can be leached from zirconia. The leaching of the yttria would allow for the spontaneous transformation from tetragonal to monoclinic which results in a drop in strength. This is similar to the hypotheses proposed by Lange et al.[22] to account for the catastrophic degradation of Y-TZP that can occur when it is treated between 1.0°C and 400°C in the presence of water vapor. They found that the Y_2O_3 reacts with the water vapor to form α-$Y(OH)_3$. The formation of this hydroxide depletes the Y_2O_3 from the tetragonal grains creating monoclinic nuclei which can grow spontaneously to transform the tetragonal grains to monoclinic. If the monoclinic grains become large enough, microcracks will develop, allowing further leaching that leads to strength degradation. Thus, "surface corrosion" of Y-TZP could be due to Y_2O_3 depletion, resulting in the spontaneous tetragonal-to-monoclinic transformation of the zirconia and a reduction in strength beyond what can be attributed to overaging alone.

Figure 4, shows the phase stability of the TZPs. The high amount of monoclinic ZrO_2 in the as-received TZPs can be attributed to the stresses placed on the surface of the bar during machining. These stresses transform the surface ZrO_2 from tetragonal to monoclinic. Subsequent treatments at 1000°C relieves the stresses allowing most of the monoclinic grains to revert to tetragonal grains.

Treated for 500 hours at 1000°C
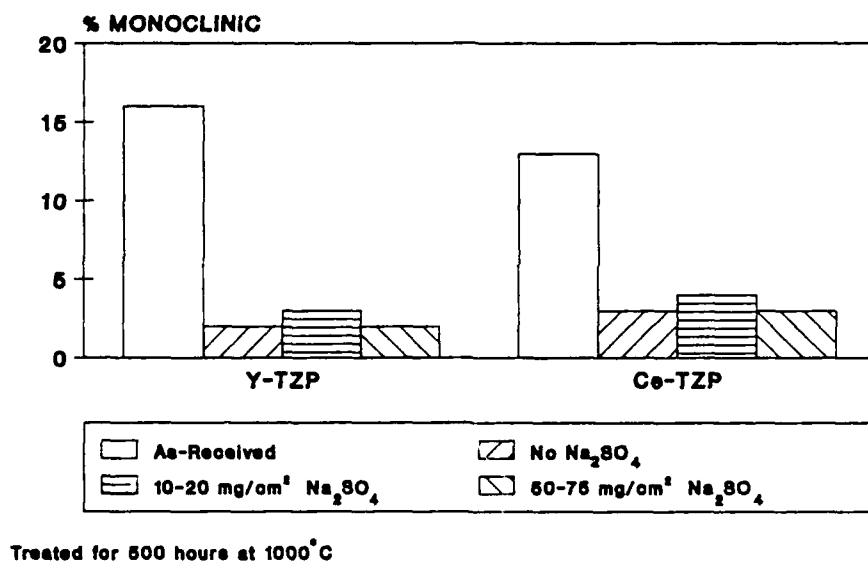
Figure 4. Surface phase stability of Y-TZP and Ce-TZP after thermal
exposure with and without sodium sulfate.

One would expect an increase in the monoclinic ZrO_2 as the Y_2O_3 was being leached from the surface. However, since this potential phenomenon only occurs in the first few layers of this fine-grai ed material, (~ 0.2 μm)[15] due to the small amount of Na_2SO_4, the resolution of the X-ray diffraction equipment is probably not sensitive enough to pick up these changes. In add flexure testing is sensitive to surface flaws rather than volume flaws. Thus, during hign temperature corrosion, the corrosive material may penetrate in and around these flaws causing al layers of grains to transform and enhancing the severity of the flaws. This potential flaw enhancement may not be discernible in routine examinations. Chemical analysis of the remaining sodium sulfate after treatment would be a more significant measure of the leaching phenomenon and resultant phase transformation.

22. LANGE, F. F., DUNLOP, G. L., and DAVIS, B. I. Degradation During Aging of Transformation-Toughened ZrO_2-Y_2O_3 Materials at 250°C. J. Am. Ceram. Soc., v. 69, no. 3, 1986, p. 237-240.

Since the Ce-TZP does not show a strength loss with the addition of Na_2SO_4, the aforementioned thermodynamic data, which indicated that ceria is more resistant to sulfation than yttria, is supported. Therefore, all things being equal, a CeO_2 stabilized zirconia should be superior to a Y_2O_3 stabilized zirconia in hot corrosion resistance. In fact, plasma-sprayed CeO_2-ZrO_2 has been patented as a protective coating for superalloys exposed to vanadium and SO_x impurities in gas turbine engines.[23]

The high purity alumina exhibited only a minor degree of strength degradation when exposed to sodium sulfate. Gannon et al.[24] found that the hot corrosion resistance of alumina refractories to molten K_2SO_4 increased with decreasing open porosity. The increased resistance was due to a reduction in the surface area available for corrosion. They also showed that control of the grain boundary chemistry played an important role in corrosion resistance. The effect of Na_2SO_4 on a glassy grain boundary phase should be similar to that of K_2SO_4 since alkali elements tend to behave similarly in silicate-based glasses. As a result, the minimal strength reduction in the alumina may be due to the corrosion of an, as yet, undetermined glassy grain boundary phase.

Examination of the fracture surfaces of the TZPs and the alumina showed that the type of strength-limiting flaw did not change after exposure to molten sodium sulfate, Figures 5 through 7. This was not the case for the Si_3N_4. It experienced an additional strength loss of ~25% when exposed to Na_2SO_4, due to a change in the flaw type and size. The typical flaw for the as-received material was machining damage, Figure 3a, and that for the bars treated without any Na_2SO_4 was oxidation pits, Figure 3b. For the bars exposed to Na_2SO_4, the flaw also a pit, but this time a corrosion pit, Figures 3c and 3d, which are on the order of 10 times larger than the oxidation pits. Analysis of the pit contents showed the presence of a small amount of Na in addition to Si and Mg. The presence of Na, as well as the glassy-like appearance of the contents of the corrosion pit, indicates that a sodium-silicate glass has been formed as outlined in Equation 5. The Mg is due to the addition of MgO as a hot-pressing aid.

Several studies have seen similar strength reductions[8,9,11] and changes in the strength-limiting flaws.[8,9] Bourne and Tressler[8] suggest that corrosion occurs due to attack of the oxide grain boundary phase, which creates the pits. X-ray analysis of the surface of the Si_3N_4 bars showed and increase in cristobalite with heat treatment time, while the addition of the sodium sulfate caused peak broadening indicating the formation of an amorphous layer, possibly a sodium-silicate glass.

For all materials, increasing the amount of Na_2SO_4 does not cause further reduction in strength. For the Y-TZP, this indicates that once a certain level of Y_2O_3 has been removed from the surface, further corrosion via this mechanism does not occur in the time frame of these tests. In the case of alumina and Si_3N_4, the grain boundary phase in each is resistant to corrosion beyond a certain level.

23. SIEMERS, P. A. and McKEE, D. W. U.S. Patent 4,328,285.
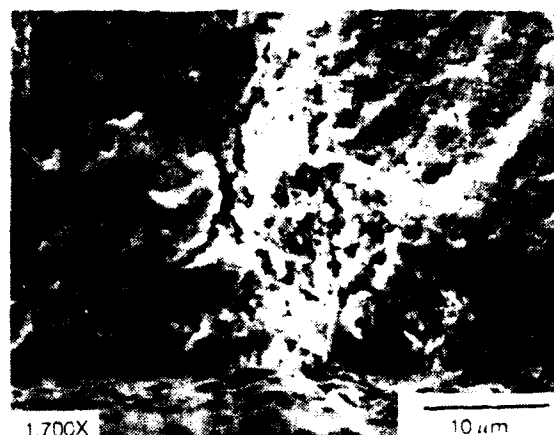24. GANNON, R. E., HALS, F. A. and REYNOLDS, H. H. *Corrosion Studies in Materials for Auxiliary Equipment in MHD Power Plants* in Corrosion Problems in Energy Conversion and Generation, C. J. Tedman, Jr., ed., Corrosion Division, The Electrochemical Society, Princeton, NJ, 1974, p. 212-224.
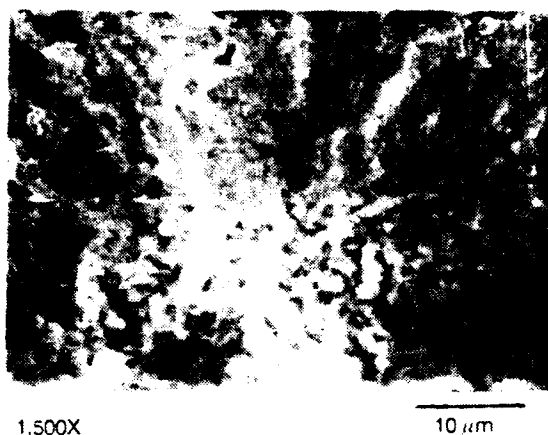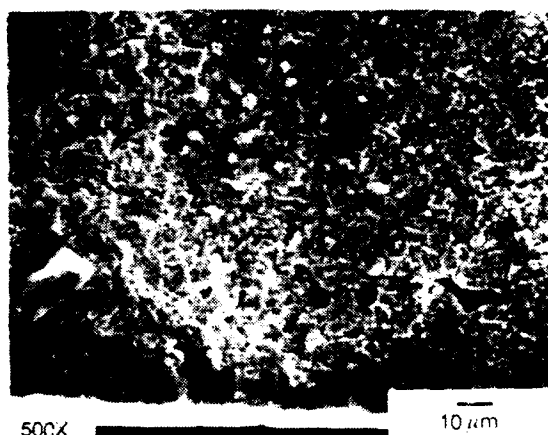
(a) As-Received   (b) After 500 Hours at 1000°C with Na_2SO_4

Figure 5. Fracture origins of Y-TZP - regions of high porosity.
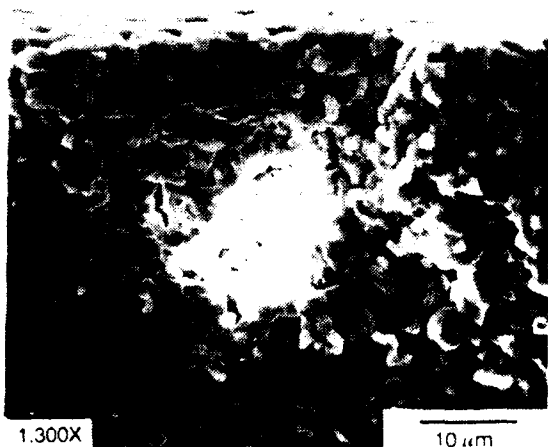

(a) As-Received   (b) After 500 Hours at 1000°C with Na_2SO_4
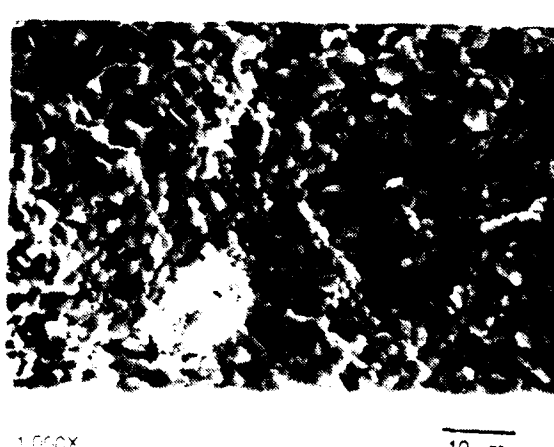
Figure 6. Fracture origins of Ce-TZP - regions of high porosity.

(a) As-Received   (b) After 500 Hours at 1000°C with Na_2SO_4

Figure 7. Fracture origins of alumina - pores.

CONCLUSION

It was found that commercially available Ce-TZP has excellent resistance to strength degradation by molten sodium sulfate when compared to a Y-TZP or a Si_3N_4. A possible mechanism of strength degradation in the Y-TZP is the Y_2O_3 depletion of the Y-TZP surface which would allow the tetragonal-to-monoclinic transformation of the zirconia to occur spontaneously, resulting in a strength reduction above that seen due to overaging alone. Strength degradation in the Si_3N_4 occurs due to the formation of large corrosion pits which may occur when the sodium sulfate reacts with the protective SiO_2 layer, allowing further attack of the oxide grain boundary phase. High purity, fully dense alumina is also very resistant to corrosion. However, it does exhibit a slight strength reduction which may be attributed to corrosion of an undetermined glassy grain boundary phase.

ACKNOWLEDGMENT

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EFFECTS OF HOT CORROSION ON THE ROOM
TEMPERATURE STRENGTH OF STRUCTURAL CERAMICS -
Jeffrey J. Swab and Gary L. Leatherman

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Ceramic materials
Zirconia
Alumina

A variety of advanced structural ceramics were treated in air at $1000°C$ for 500 hours with and without various amounts of sodium sulfate. Room temperature flexure strength was determined before and after treatments. Results show that Ce-TZP and alumina are resistant to strength degradation after exposure to sodium sulfate, however Si_3N_4 and, to a lesser degree, Y-TZP are not. The Y-TZP had a strength loss of ~25% after 500 hours at $1000°C$ with 10 to 20 mg/cm^2 of Na_2SO_4. This loss is about 10% greater than that experienced by specimens when treated at $1000°C$ for 500 hours without sodium sulfate present, and is probably due to the leaching of Y_2O_3 from the zirconia which allows the tetragonal zirconia to transform to the monoclinic phase. Under similar conditions, the silicon nitride experienced a loss of ~65% when sodium sulfate was added. This strength loss is ~25% greater than the loss after thermal exposure in the absence of sodium sulfate. The additional strength loss here is due to the formation of larger corrosion pits.